

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Stabilized Polyamide Compositions

We, TOYO BOSEKI KABUSHIKI KAISHA, a corporation organised under the laws of Japan, of 8, 2-chome, Dojima-hama-dori, Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for stabilizing a polyamide, to impart thereto resistance against thermal deterioration.

Generally, a polyamide is sensitive to oxidation and when subjected to elevated temperature (for instance a high temperature such as is often encountered during its service by a polyamide used for reinforcing rubber) in the presence of oxygen, it may manifest such defects as a lowering of the degree of polymerization, discoloration, embrittlement or cross-linking. Various methods for stabilizing have previously been proposed for preventing such thermal deterioration of a polyamide.

One previous proposal is to blend a small amount of a heavy metal compound, e.g. copper compound with a polyamide, but there is still a room for improvement from the practical viewpoint.

The reason why a copper compound is effective is, as explained by J. R. KOCHI in J.A.C.S., 84, 1572, that a peroxide produced in a polyamide is decomposed by Cu²⁺; since copper per se reversibly changes between monovalent and divalent, the reaction appears to be due to a functional mechanism wherein the half-value period as a thermal stabilizer is long.

It appears therefore that, in order that the added copper compound may develop thermal stability, it must be dissolved in the form of molecule or ion in a polyamide. If the copper compound decomposes, and separates into elemental copper or copper oxide, the thermal

stability will completely disappear. Furthermore, in consequence of the separation there may result filament breaking upon spinning, and staining of the filament.

Another problem which arises in the use of a copper compound is corrosion of the apparatus. Normally, a copper compound especially at high temperatures corrodes a metal which is more ionizable than copper, by ion exchange, the anion (or ligand) of the copper compound corroding the metal by elution in the form of a salt.

Thus, a main object of this invention is to provide a method of stabilizing polyamides against thermal deterioration, using a form of copper as the stabiliser.

According to the present invention there is provided a process for stabilizing a polyamide which comprises incorporating in the polymer, or in a precursor thereof prior to polymerisation, from 0.001 to 1% by weight (calculated as copper) of a pre-formed complex of a copper (II) salt and a lactam or a complex of a copper (II) salt and an ω -amino acid, the lactam or ω -amino acid moiety of said complex containing 5 to 12 carbon atoms.

The copper complex used in this process can easily be prepared by heating a mixture of a copper salt and a lactam having 5—12 carbon atoms or an ω -amino acid having 5—12 carbon atoms to an elevated temperature (e.g. 100—140°C.). The copper salt is preferably soluble in the lactam or amino acid used. Examples thereof are inorganic copper salts such as the sulfate, chloride and bromide and organic copper salts such as the acetate, stearate and salicylate. The preferred lactam or ω -amino acid has 5—8 carbon atoms, and examples are: valerolactam, caprolactam, enantholactam, capryllactam, ω -amino valeric acid, ω -amino caproic acid, ω -amino enanthic acid and ω -amino caprylic acid.

It should be noted that the complex must

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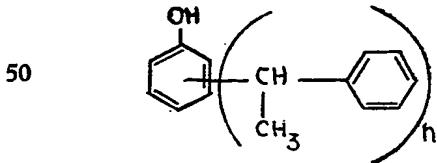
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- be pre-formed, i.e. cannot be formed within an unpolymerised precursor of the polyamide. The use of copper salts as stabilisers for polyamides, by addition thereof to a monomer e.g. ϵ -caprolactam has been previously disclosed, but use of the complex formed before it is added to the monomer gives a more predictable stability.
- The preparation of the copper complex, exemplified with reference to ϵ -caprolactam, proceeds as follows:
- To 100 parts by weight of ϵ -caprolactam were added 20 parts by weight of cupric chloride. The resultant solution was heated to about 120°C., and kept at that temperature for 2 hours. During the heating, the solution gradually changed to green. To the green viscous solution thus obtained benzene was added and when the mixture was left to stand, plate-like and aculeate crystals were obtained. From the obtained crystals, 4 kinds of copper complexes having different colors were isolated. The melting points of these complexes were within the range of 185—186°C. The blending of the copper complex with a polyamide may be carried out before, during or after the polymerization of a polyamide, but it is preferred to add the stabilising complex to the polymer.
- For the process of this invention, the copper complex does not have to be purified and isolated. It is also possible to add the solution obtained by said reaction wherein the complex coexists with excess ligand (i.e. lactam or amino acid) to a polyamide material.
- It has been found that sometimes it is advantageous to add the complex together with styrenated phenol in an amount of up to 600% by weight, especially 50—600% by weight based on the weight of the complex. In such cases it is possible to blend the complex as a solution in styrenated phenol with a polyamide. Further, it is possible for the preparation of said complex to be carried out in the presence of styrenated phenol and the obtained reaction solution to be added to a polyamide.
- (Styrenated phenol is a mixture of compounds of the formula:



wherein n is 1, 2 or 3; a mixture consisting of about 35% by weight monostyrenated phenol and about 50% by weight tristyrenated phenol, about 15% by weight distyrenated phenol is commercially available as "Antigen S." (trade name: Simitomo Chemical Co., Ltd.).

Styrenated phenol acts as a thickening agent to adjust the viscosity of the complex feed and it is considered that it will partially dissociate to styrene and phenol at temperatures such as 200°C. or higher and prevent an undesirable deposit of CuO.)

The lactam-copper complex and the amino acid-copper complex can effectively prevent the thermal deterioration of polyamide. The copper complex used in this invention has a heat stability as a thermal stabilizer of a polyamide superior to heat stability of hitherto known copper compounds and separates hardly at all into elemental copper or copper oxide in a molten polyamide.

In a preferred embodiment of this invention, said copper complex is blended with the polyamide together with a quaternary organic base halide in an amount of up to 300% by weight, preferably 50 to 300% by weight based on the weight of said complex. It has been found that a quaternary organic base halide effectively inhibits the metal corrosion of the copper complex.

As a quaternary organic base halide, one that has a quaternary nitrogen atom with one or two of the hydrocarbon radicals bonded thereto being alkyl radicals having 10—22 carbon atoms, is preferable. As examples of said halide, there are cetyltrimethylammonium bromide, cetylpyridinium bromide, stearyltrimethylammonium chloride and distearyltrimethylammonium iodide. As a halogen, iodine is most effective and the effect tends to decrease in the sequence of bromine and chlorine. However, as shown in Examples, in the case of using chlorides, the effect of preventing corrosion is good.

It has also been found that the corrosion prevention action of a quaternary organic base halide is synergistically enhanced by a primary, secondary or tertiary amine. Suitable organic amines have relatively high boiling points. Amines whose boiling points are lower than the melting point of the polyamide by more than 100°C. are unsuitable since they are apt to vaporise while the polyamide is melt-formed.

As examples of suitable organic amines, there may be cited, quinoline, morpholine, piperidine, N,N-dimethylaniline, diethyltri-amine, hexamethylenediamine, monoethanol-amine, diamino-diphenylmethane, palmityl-amine, and stearylamine, however, especially higher aliphatic amines having high boiling points are preferable. The amount of amine used may be up to 300% by weight, particularly 50—300% by weight based on the copper complex.

Polyamides which can be stabilized by this invention include, aliphatic polyamides, obtained from lactams, hexamethylenediammonium adipate and/or hexamethylenediammonium sebacate; aromatic polyamides obtained

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from meta-xylylenediammonium adipate, meta-xylylenediammonium sebacate, meta-para-xylylenediammonium adipate (para content within 50%), hexamethylenediammonium terephthalate or a mixture thereof or a mixture thereof with aliphatic nylon salts.

It should be understood that when the copper compound is used as a thermal stabilizer of these polyamides, alkali metal halides which have hitherto been used in combination such as, for instance, potassium iodide, sodium iodide, potassium bromide and sodium bromide may be used together with the copper complex of this invention.

The present invention may be further illustrated by the following examples. Unless particularly defined, part expresses part by weight.

EXAMPLE 1

A solution consisting of 100 parts of caprolactam and 13 parts of cupric chloride was heated to 120°C. with stirring for 2 hours. 0.28 part of the obtained green transparent solution was uniformly mixed with 100 parts of molten 6-nylon (number average molecular weight: about 22,000). By melt spinning at a spinning temperature of 300°C. and a winding speed of 500 m/min. and by drawing at 185°C. with a draw ratio of 4.55 of said mixture, a white filament having a tensile strength of 8.9 g/de. and a break elongation of 21% was obtained. After the filament was exposed in air at 180°C. for 20 hours, the tensile strength of it was 7.8 g/de., which means that lowering of tensile strength due to this exposure was about 12%.

The filament prepared under the same conditions except the copper complex was not contained showed loss of tensile strength due to exposure in air at 180°C. for 20 hours of about 85%.

EXAMPLE 2

A solution consisting of 100 parts of aminocaproic acid and 20 parts of cupric acetate was heated to 130°C. for 2 hours. After the reaction mixture was cooled, it was poured into benzene. As a result green aculeate crystals were obtained. 0.3 part of this complex was added to 100 parts of caprolactam and to the mixture was added 0.3 part of water, 0.3 part of acetic acid and 0.1 part of potassium iodide. The mixture was subjected to a polymerization temperature of 260°C. for 15 hours, as a result 6-nylon having a number average molecular weight of 15,000 wherein was incorporated the copper complex was obtained. From this polymer composition, by melt spinning at 280°C. and a winding speed of 480 m/min. and by drawing at a drawing temperature of 185°C. and a draw ratio of 4.55, filament was prepared. The filament breaking of it was 0.01 time an hour. The loss of tensile strength of the filament due to exposure in air at 180°C. for 20 hours was 10%.

For the sake of comparison, the foregoing

operations were repeated except 0.2 part of cupric acetate was used instead of 0.3 part of the copper complex. In this case, the filament breaking was 0.1 time an hour and in the nozzle slight precipitation of metal copper was observed. The loss of tensile strength of the filament due to exposure in air at 180°C. for 20 hours was 22%.

EXAMPLE 3

A solution of 12.5 parts of cupric chloride in a mixture of 70 parts of caprolactam and 30 parts of styrenated phenol was heated with stirring at 120°C. for 2 hours to give a transparent dark green solution. 0.4 Part of said solution was mixed with 100 parts of chips of polycaproamide (number average molecular weight: 21,000). The chips were melted and extruded at 295°C. and a winding speed of 450 m/min. to form filament. Said filament was drawn at a drawing temperature of 185°C. and a draw ratio of 4.55. The loss of (tensile) strength of the obtained filament due to exposure in air at 180°C. for 20 hours was 8%.

EXAMPLE 4

From chips of nylon 66 (number average molecular weight: 20,000) wherein 0.3 part of the green transparent solution of the lactam-copper complex in Example 1 was mixed with 100 parts of the nylon chips, by melt spinning at a spinning temperature of 290°C. and a winding speed of 400 m/min. and by drawing at 185°C. and a draw ratio of 4.55, filament was prepared. The lowering of tensile strength of the obtained filament due to exposure in air at 180°C. for 20 hours was 10%.

The foregoing operations were repeated except chips of poly(m-xyleneadipamide) (number average molecular weight: 21,000) was used instead of the chips nylon 66 and the melt spinning was carried out at 290°C. and a winding speed of 400 m/min. The loss of tensile strength of the obtained filament due to exposure in air at 180°C. for 20 hours was 9%.

EXAMPLE 5

A solution of 20 parts of cupric chloride in 100 parts of caprolactam was heated to 120°C. for 2 hours. To the obtained green solution was added excess benzene to salt out green crystals and the crystals were separated. 20 Parts of the obtained green crystalline complex were dissolved in 100 parts of styrenated phenol. The obtained solution was heated to 250°C. for 1 hour, however, no precipitation of metal copper was recognized. Whereas, a solution of 20 parts of cupric salicylate in 100 parts of styrenated phenol was heated to 250°C., precipitation of metal copper started after 2 minutes.

20 Parts of said caprolactam-copper complex and 20 parts of cetyltrimethylammonium chloride were dissolved in 100 parts of styrenated phenol. Into 20 g of said solution a 3 × 0.7 × 0.1 cm stainless steel (SUS 33) piece was immersed and heated to 260°C. for

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- 24 hours. The weight loss of the stainless steel was 0.10%. 65
- In a similar test concerning a solution of 5 parts of the caprolactam-copper complex in 120 parts of styrenated phenol, the weight loss of the stainless steel piece was 2.83%, and the surface of the sample slightly corroded.
- Molten polycaproamide (number average molecular weight: 22,500) was mixed with 0.3 part based on 100 parts of the polymer of said solution of 20 parts of the caprolactam-copper complex and 20 parts of cetyltrimethylammonium chloride in 100 parts of styrenated phenol. From said melt, by melt spinning at a spinning temperature of 295°C. and a winding speed of 490 m/min. and by drawing at a drawing temperature of 185°C. and a draw ratio of 4.55, white filament was prepared. The loss of tensile strength of this filament due to exposure in air at 180°C. for 20 hours was 11%. 70
- To 100 parts of caprolactam were added 25 16 parts of cupric chloride and 28 parts of cetyltrimethylammonium bromide, and the mixture was heated to 120°C. with stirring for 2 hours. In 20 g of the obtained transparent green solution a thin piece of SUS 33 (3 × 0.7 × 0.1 cm) was heated to 260°C. for 24 hours. The weight loss of the SUS material was 0.15%. 75
- To a melt of polycaproamide (number average molecular weight: 22,500) was mixed 30 0.2 part of said green solution based on 100 parts of the polymer. From said mixture, by melt spinning at a spinning temperature of 295°C. and a winding speed of 510 m/min. and by drawing at 185°C. and a draw ratio of 4.55, a white filament was prepared. The loss of tensile strength of this filament due to exposure in air at 180°C. for 20 hours was 12%. 80
- EXAMPLE 6**
- To 100 parts of caprolactam were added 35 16 parts of cupric chloride and 28 parts of cetyltrimethylammonium bromide, and the mixture was heated to 120°C. with stirring for 2 hours. In 20 g of the obtained transparent green solution a thin piece of SUS 33 (3 × 0.7 × 0.1 cm) was heated to 260°C. for 24 hours. The weight loss of the SUS material was 0.15%. 85
- Chips of nylon 66 (number average molecular weight: 19,000) were mixed with 0.25 part of said dark red solution of the complex. From the chips, by spinning at a spinning temperature of 290°C. and a winding speed of 530 m/min. and by the drawing whose conditions were same as those of the above, white filament was obtained. The loss of tensile strength of the filament due to exposure in air at 180°C. for 20 hours was 11%. 90
- Chips of poly(m-xylylenediamine adipate) (number average molecular weight: 19,500) were mixed with 0.25 part based on 100 parts of the polymer of said dark red solution of the complex. From the chips, by melt spinning at a spinning temperature of 280°C. and a winding speed of 450 m/min., a white filament was prepared. The drawing conditions were same as those of the foregoing. The loss of tensile strength of the filament due to exposure in air at 180°C. for 20 hours was 10%. 95
- EXAMPLE 8**
- A solution consisting of 100 parts of ω -aminocaproic acid, 20 parts of cupric acetate, 30 parts of stearyltrimethylammonium chloride was heated to 130°C. with stirring for 2 hours. 0.2 part of the obtained complex solution was added to 100 parts of ϵ -caprolactam, and the mixture was further mixed with 0.3 part of water, 0.3 part of acetic acid and 0.1 part of potassium iodide. The resultant mixture was maintained at a polymerization temperature of 260°C. for 15 hours, and a polymer having a number average molecular weight of 15,000 was obtained. By spinning said polymer at a spinning temperature of 290°C. and a winding speed of 530 m/min., a white filament was obtained. The drawing conditions employed were same as those of the foregoing Examples. The loss of tensile strength of the filament due to exposure in air at 180°C. for 20 hours was 10%. 100
- Said spinning operations were continued for one week, but no corrosion was observed at the nozzle. On the contrary, in the case wherein stearyltrimethylammonium chloride was not blended, a slight corrosion was observed at the nozzle. 110
- EXAMPLE 9**
- A solution consisting of 100 parts of caprolactam, 20 parts of cupric chloride, 40 parts of cetyltrimethylammonium iodide and 25 parts of styrenated phenol was heated to 120°C. with stirring for 2 hours to give a dark red transparent solution. In 20 g of said solution a thin SUS 33 piece was immersed and the solution was heated to 260°C. for 125
- A melt of polycaproamide (number average molecular weight: 21,500) was mixed with 0.2 part of said dark red solution. From the melt, by melt spinning at a spinning temperature of 295°C. and a winding speed of 500 m/min. and by drawing at a drawing

- 24 hours, however, no separation of metal copper was observed. The weight loss of the SUS material due to this treatment was only 0.05 %. A melt of nylon 6 (number average molecular weight 20,000), was mixed with 0.2 part of said dark red solution based on 100 parts of the polymer. The melt was extruded at a spinning temperature of 295°C. and a winding speed of 450 m/min. as filament. Subsequently, the filament was drawn as in the preceding Examples, and a white filament was obtained. The loss of tensile strength of the filament due to exposure in air at 108° for 20 hours was about 10%.
- 5 molecular weight 20,000), was mixed with
10 0.2 part of said dark red solution based on
 100 parts of the polymer. The melt was ex-
 truded at a spinning temperature of 295°C.
 and a winding speed of 450 m/min. as fila-
 ment. Subsequently, the filament was drawn

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EXAMPLE 10
From the components whose amounts (parts by weight) are shown in the following Table 1, 4 kinds of stabilizer solutions A, B, C and D were prepared.

TABLE 1

Solution	A	B	C	D
Caprolactam	100	120	105	125
Cupric chloride	10	10	10	10
Cetyltrimethylammonium chloride	20	0	20	0
Palmityl amine	5	5	0	0
Total	135	135	135	135

In each case, a solution of 10 parts of cupric chloride in 100 parts of lactam was heated to 120°C. with stirring for 2 hours, and to said solution the residual lactam and/or cetyltrimethylammonium chloride, palmityl amine were added. A thin stainless steel piece (3 × 0.7 × 0.1 cm) was immersed in each solution, and the solution was heated to 260°C. in a nitrogen atmosphere for 24 hours. The kind, initial weight, final weight, loss of weight (in g) and loss of weight (in %) of the stainless steel were shown in Table 2.

5 (3 × 0.7 × 0.1 cm) was immersed in each
 solution, and the solution was heated to 260°C.
 in a nitrogen atmosphere for 24 hours. The
 kind, initial weight, final weight, loss of weight
 (in g) and loss of weight (in %) of the stain-
 less steel were shown in Table 2.

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TABLE 2

Corroding action of stabilizer solution on stainless steel

Stainless steel	Stabilizer composition	Initial weight (g)	Final weight (g)	Loss of weight (g)	Loss of weight (%)
SUS 21	A	1.8248	1.8003	0.0245	1.34
	D	1.7391	1.5848	0.1543	9.87
SUS 27	A	1.7084	1.7072	0.0012	0.07
	D	1.8527	1.8464	0.0063	6.34
SUS 33	A	1.7832	1.7829	0.0003	0.02
		1.7756	1.7752	0.0004	
SUS 33	B	1.8148	1.8048	0.0100	0.53
		1.7952	1.7866	0.0092	
SUS 33	C	1.7817	1.7792	0.0025	0.12
		1.7901	1.7883	0.0018	
SUS 33	D	1.7913	1.7376	0.0537	2.95
		1.8019	1.7526	0.0523	

POOR QUALITY

A melt of polycaproamide (number average molecular weight: 19,300) was mixed with said solution A in an amount of 0.32 part based on 100 parts of the polymer. By melt spinning the melt at a spinning temperature of 290°C. and a winding speed of 500 m/min., and by drawing same as in the preceding Examples, a white filament was prepared. The loss of tensile strength of the filament due to exposure in air at 180°C. was 9%. Said spinning operations are continued for one week, but no corrosion was observed at the nozzle.

EXAMPLE 11
By carrying out the reaction same as in the

preceding Example 10, from 100 parts of caprolactam and 10 parts of cupric chloride, a complex solution was prepared, to which were added 20 parts of cetyltrimethylammonium chloride and 5 parts of organic amines shown in the following Table 3, whereby stabilizer solution were prepared.

The result of corrosion tests by the stabilizer solution of SUS 33 carried out as in Example 10 and the loss of tensile strength due to exposure in hot air of polycaproamide filament prepared as in Example 10 by using each stabilizer solution were shown in the following Table 3.

TABLE 3

Organic amine	Initial weight (g)	Final weight (g)	Loss of weight (%)	Loss of tensile strength after exposure at 180°C. for 20 hours
Palmityl amine	1.8014	1.8010	0.02	9%
Stearyl amine	1.8235	1.8231	0.02	11%
Monoethanolamine	1.8001	1.7911	0.05	10%
Morpholine	1.8333	1.8229	0.02	11%
None	1.7945	1.7923	0.12	12%

30 WHAT WE CLAIM IS:—

1. A process for stabilizing a polyamide which comprises incorporating in the polymer, or in a precursor thereof prior to polymerization, from 0.001 to 1% by weight (calculated as copper) of a pre-formed complex of a copper (II) salt and a lactam or a complex of a copper (II) salt and an ω -amino acid, the lactam or ω -amino acid moiety of said complex containing 5 to 12 carbon atoms.
2. A process as claimed in claim 1, in which the complex is added to the polyamide together with up to 300% by weight, based on the copper complex, of a quaternary organic base halide.
3. A process as claimed in claim 2, in which an organic amine having a boiling

point not less than 100°C. below the melting point of the polyamide is also added to the polyamide.

4. A process as claimed in any preceding claim, in which the copper salt in the complex is cupric chloride.

5. A process according to claim 1, substantially as hereinbefore described.

6. A polyamide composition stabilized by a process as claimed in any preceding claim.

7. A composition according to claim 6, which includes up to 600% by weight, based on the copper complex, of a styrenated phenol.

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